Indian J. Phys. **48**, 225–235 (1974).

Infrared spectra of potassium citrate monohydrate single crystals

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(*Received 5 January* 1973)

The infrared spectra of potassium citrate monohydrate single crystals (001, 010 plates) have been recorded in the region 400–4000 cm^{-1} using a Perkin-Elmer, infrared spectrophotometer, model 337 with a double grating dispersing unit. The free state frequencies of the citrate ion were taken from the reported works of Rao & Swamy (1970, 1971, 1972*a*, 1972*b*) and the observed frequencies in the present spectra were assigned to different modes of vibration of the citrate ion in the unit cell. The spectra were analysed according to the standard procedures of Halford (1946) and Hornig (1948). The splittings of the frequencies revealed that the citrate ion must have an approximate C_s site symmetry in the unit cell. Thus sixty one out of the ninety six expected fundamental frequencies of the citrate ion in the potassium citrate monohydrate unit cell are identified in the spectra and assigned to their respective species. The hydrogen bond frequency range has been identified according to the details given by Hadzi (1965). The effect of orientation of the ions in the unit cell has been discussed with reference to the spectra of different crystal plates.

1. Introduction

The work done on the molecular structure of the citrate ion is very meagre and hence the authors have taken up this work. So far the authors have reported the tentative analysis of the infrared spectra of anhydrous citric acid (Rao & Swamy 1970), sodium citrate and ammonium citrate (Rao & Swamy 1971), lithium citrate tetrahydrate (Rao & Swamy 1972*a*), and potassium citrate monohydrate (Rao & Swamy 1972*b*). As a continuation the authors now have recorded the infrared spectra of potassium citrate monohydrate single crystals and an assignment of the observed frequencies is reported in this paper. Prior to the present work there is only one paper by Duval (1962) on the infrared spectrum of potassium citrate monohydrate which did not report any analysis. The common frequencies in the polycrystalline spectra of these compounds were taken as the free state frequencies of the citrate ion. Using this set of frequencies

of the citrate ion, the analysis of the frequencies in the single crystal spectra of potassium citrate monohydrate has been carried out.

2. Experimental

Potassium citrate monohydrate of B.P. grade was procured from Eagle Pharmaceuticals and purified by repeated recrystallization. Single crystals were grown from a saturated solution of the substance in distilled water, at room temperature. The crystal has a cleavage plane identified to be (001). Accordingly, (001) specimen plates were obtained by cleaving and grinding the cleaved plate over a slightly undersaturated aqueous solution of the salt. The (010) face is grown naturally which is identified from the morphological details given by Groth (1910). The axes identification was confirmed by taking X-ray oscillation rotation photographs of (010) and (001) plates. Then the infrared spectra of (001) and (010) plates were recorded which are reproduced in figures 1, 2 and 3. The observed frequencies with assignments are given in table 2 and the citrate ion frequencies for comparison are given in table 1.

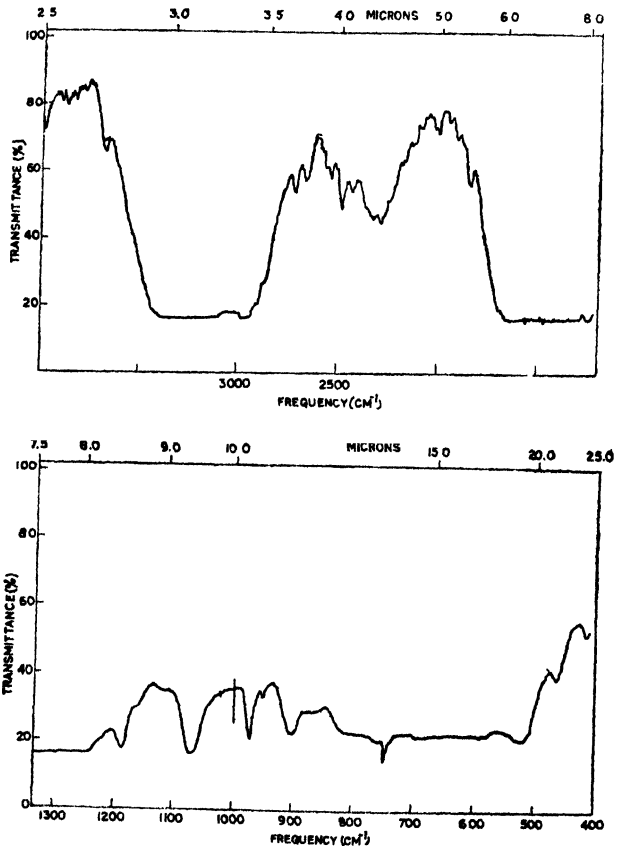

Fig. 1. Infrared spectrum of potassium citrate monohydrate-single crystal (010) plate spectrum. 4000–400 cm^{-1} region using PEIRS, Model 337-Double beam instrument Grating dispersing unit.

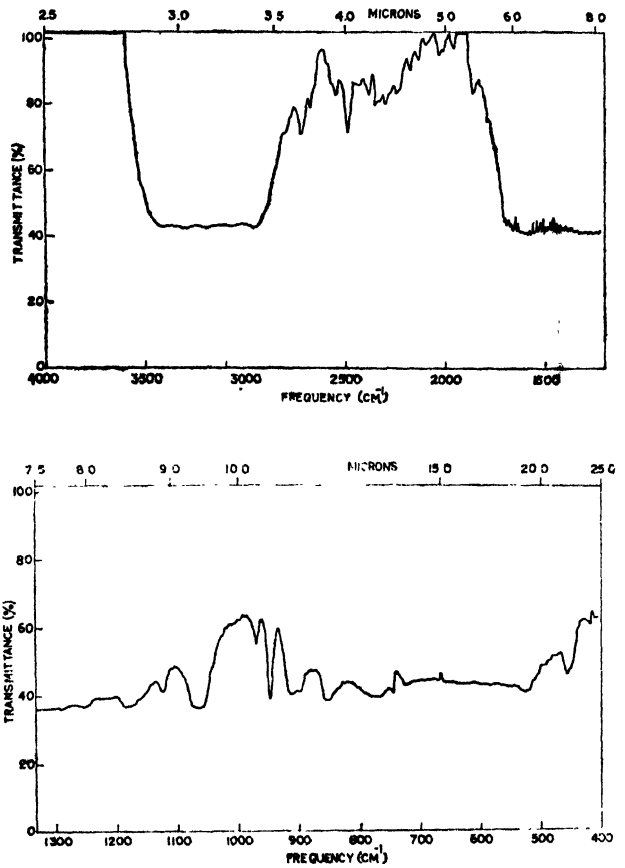

Fig. 2 Infrared spectrum of potassium citrate monohydrate-single crystal spectrum—*b*-axis parallel to slit of the spectrophotometer—4000–400 cm^{-1} region using PEIRS, model 337–Double beam instrument-Grating dispersing unit.

3. Results and Discussion

It is known from Burns & Iball (1957) and Love *et al* (1960) that potassium citrate monohydrate crystallizes in the monoclinic system with four molecules in its unit cell of dimensions $a = 7.06$A, $b = 11.72$A, $c = 13.69$Å, and $\beta = 112.0°$ and has a space group C^5_{2h}. Full structural details are not available for this compound to know anything about the structure of the citrate ion in the unit cell. However, the structure of the citrate ion in magnesium citrate decahydrate crystal is known from the details given by Johnson (1965). According to this, citrate ion has only C_1 site symmetry in the crystal unit cell. Data on the bond lengths and bond angles of different bonds in the citrate ion from the details given by Johnson has been quoted in our earlier paper (Rao & Swamy 1972*b*). The C_1 point group symmetry of the citrate ion could be inferred from the spectroscopic observations as follows.

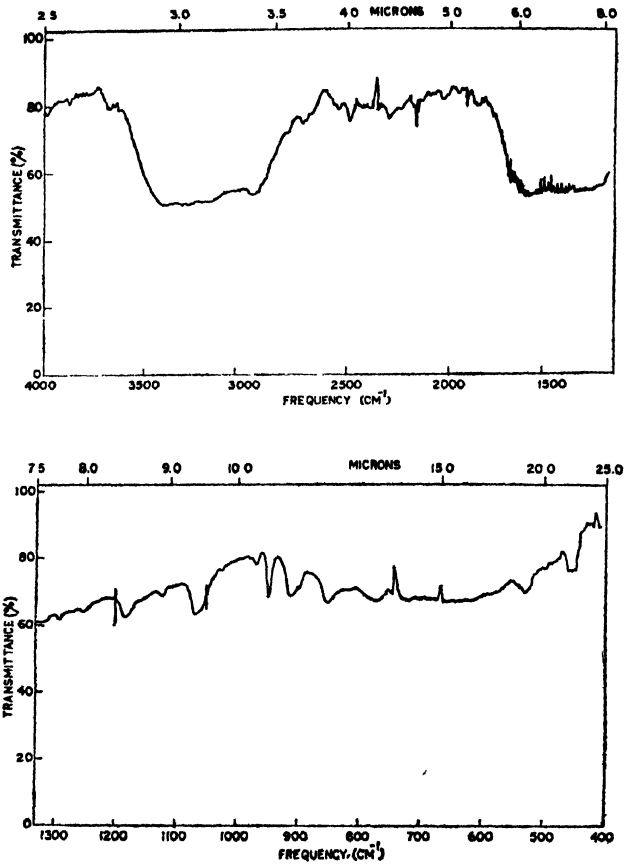

Fig. 3 Infrared spectrum of potassium citrate monohydrate-single crystal (001) plate spectrum—a-axis parallel to slit of the spectrophotometer-4000–400 cm^{-1} region using PEIRS, model 337-Double beam instrument—Grating dispersing unit.

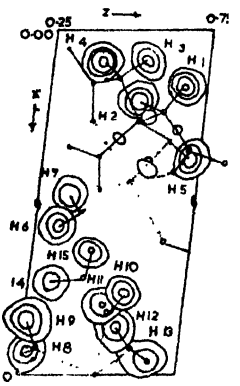

Fig. 4a Magnesium tricitrate unit cell-viewed along the b-axis.

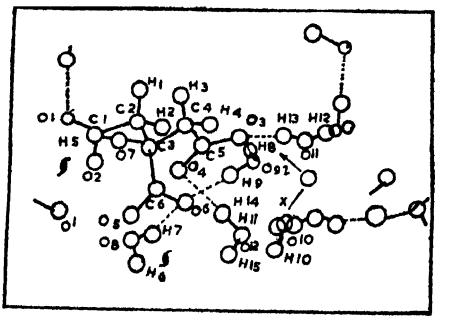

Fig. 4b Hydrogen bonding and molecular-packing in the magnesium tricitrate unit cell viewed along the b-axis.

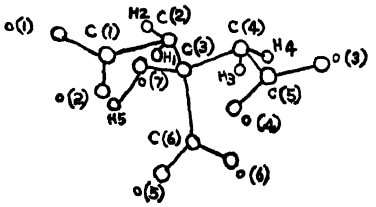

Fig. 5 Structure of the tricitrate ion $(C_6H_5O_7)^{---}$

Table 1. Infrared frequencies of the citrate ion in the free state (taken from polycrystalline studies) in comparison to the frequencies of the citrate in the solid state from single crystal spectra

Polycrystalline		Freq. number	Single Crystal		Assignment
Freq. cm^{-1}	Int.		Freq. cm^{-1}	Species	
2937	vs	ν_3	2940 2928	b_u a_u	$3H_2$ asymm. stretch.
2895	s	ν_1	2900 2878	a_u b_u	CH_2 symm. stretch.
1572	m.	ν_8	1574 1566	b_u a_u	COO asymm. stretches.
1549	m.	ν_9	1555 1548	a_u b_u	
1532	m.	ν_{10}	1541 1533	b_u a_u	
1501	m.	ν_{17}	1502 1490	a_u b_u	CH_2 bends.
1480	m.	ν_{18}	1487 1477	a_u b_u	
1465	m.	ν_5	1472 1464	a_u b_u	COO symm. stretches.
1445	m.br.	ν_6	1455 1444	a_u b_u	
1420	m.	ν_7	1433 1420	a_u b_u	
1406	m.sh.	ν_{13}	1413 1395	a_u b_u	CH_2 bends.
1340	m.br.	ν_{35}	1346 1333	a_u b_u	CH_2 deformations.
1285	m.br.	ν_{36}	1295 —	— —	
1182	w.	ν_{11}	1189 1183	a_u b_u	C–OH stretch.

Table 1 contd.

Polycrystalline		Freq. number	Single Crystal		Assignment
Freq. cm^{-1}	Int.		Freq. cm^{-1}	Species	
1071	m	ν_{27}	1075	b_u	C–OH oscillations.
			1069	a_u	
1065	w.	ν_{28}	1065	b_u	
			1057	a_u	
969	w	ν_{12}	970	b_u	C–C stretches.
			—	—	
950	w	ν_{13}	950	b_u	
			945	a_u	
914	s	ν_{21}	917	a_u	COO deformations.
			911	b_u	
900	s	ν_{22}	900	a_u	
			—	—	
856	m	ν_{23}	860	b_u	
			856	a_u	
842	m	ν_{24}	849	a_u	
			842	b_u	
770	w	ν_{40}	777	—	CH_2 rockings.
			764	—	
747	vw	ν_{41}	749	—	
			744	—	
		ν_{29}	535	—	
			528	—	
		ν_{30}	523	—	C–C bendings.
			511	—	
		ν_{31}	505	—	
			495	—	
		ν_{37}	468	—	COO out of plane bendings.
			462	—	
		ν_{38}	460	—	
			453	—	
		ν_{42}	428	—	C–C torsions.
			419	—	
		ν_{43}	420	—	
			411	—	

From the available data on the infrared and Raman spectra of sodium citrate, the authors observed that many of the groups of frequencies are occuring in both the spectra. This is possible only when the citrate has C_{2v}, C_1 etc., point groups. Apart from this the observed infrared frequencies in the spectra of potassium citrate monohydrate single crystals could be satisfactorily explained only when we take C_1 point group for the free citrate ion. Thus we were lead by the above facts to the conclusion that C_1 must be the point group of the free

citrate ion. The citrate ion has eighteen atoms and must have forty eight frequencies. The number of frequencies of different bond stretchings, bendings etc., were calculated according to the procedure of Decius (1949). The common infrared frequencies in the spectra of sodium citrate potassium citrate, ammonium citrate and lithium citrate tetrahydrate were noted. These frequencies should belong to the citrate ion having C_1 point group symmetry. The frequencies are assigned to their respective groups using the tables for the characteristic group frequencies. The frequencies are numbered $\nu, \nu_{12}, \ldots, \nu_{48}$. In assigning the frequencies to ν_1 etc., there was some difficulty regarding assignment whenever two groups of frequencies are very near and this difficulty was overcome by observing the single crystal spectra of potassium citrate monohydrate. Thus the free state citrate ion frequencies have been identified and are given in table 1. We have identified thirty one fundamental frequencies out of forty eight that are theoretically expected. Using this set of frequencies of the citrate ion, the infrared spectra of potassium citrate monohydrate single crystals were subjected to an analysis as given below.

From the available structural data on (Burns & Iball 1954) potassium citrate monohydrate and the symmetry of the free citrate ion, we can conclude that the site of symmetry of citrate ion in the potassium citrate monohydrate crystal must be C_1. According to the details given by Johnson (1965) on the structure of the citrate ion in the unit cell of magnesium citrate decahydrate, all the atoms of the ion are arranged on two planes which are nearly perpendicular to each other. The fine structure and specially the splitting of the fundamental frequencies in the spectrum reveal the fact that the citrate ion may be considered to have an approximate site symmetry C_s *i.e.*, the citrate ion may be considered approximately to consists of two C_s groups (considering the atoms on each plane forming a C_s group and the two groups being perpendicular to each other the interaction will be negligible). The observed frequencies are assigned accordingly and discussed below. The correlation table between C_1 (the point group), C_d (site group) and C_{2h} (space group) is given in table 2.

According to the orientations of the citrate ions in the unit cell as reported by Johnson (1965) for magnesium tricitrate it is concluded that T_x, T_y, T_z, the dipole moment transition vectors, are parallel to c, a and b crystallographic axes respectively, and T_x, T_y are of b species and T_z is of a species. According to the selection rules a and b species are only permitted in the infrared. Therefore in the (010) plate spectrum it is expected that only b species should be present and in the (001) plate spectrum both a and b species should be present.

A free state fundamental like ν_1 will split into four components due to the presence of four molecules in the unit cell. According to the correlation table 2 only two frequencies of a and b species appear in the infrared, out of the four

Table 2. Infrared frequencies of potassium citrate monohydrate in the (*a*) KBr pellet spectrum and in the (*b*) single crystal spectra of (*i*) (010) symmetry plate (*ii*) (001) symmetry plate with *b*-axis parallel to the slit of the spectrophotometer (*iii*) (001) symmetry plate with *z*-axis parallel to the slit of the spectrophotometer.

I.R. freq.cm^{-1} KBr pellet spectrum due to authors	Int.	Single crystal I.R. freq.cm^{-1} (010) plate	Int.	Species	Single crystal I.R. freq.cm^{-1} (001) plate *b*-axis	Int.	Species	Single crystal I.R. freq.cm^{-1} (001) plate *a*-axis	Int.	Species	Assignment
		3779	vvw					3675	vvw		
3663	m	3687	w.br					3650	vvw		O–H stretch water of crystallisation.
3560	vs	3672	w.br		3425	vs		3400	s.br		
3450		3390	br.ab		3300	vs		3300	s.br		
3125	vs.br	—	—		—	—					
2937	vs	2940	s	b_u	2928	vs	a_u	2940	s	b_u	ν_3.CH_2 asymm. stretch.
2895	s	2878	s	b_u	2900	vs	a_u	2900	m	a_u	ν_1.CH_2 symm. stretch.
								2878	m	b_u	
								—	—		
2370	w	2360	m		2380	w					
2350	w	2325	m		2350	w					OH stretches lowered due to hydrogen bonding.
					2322						
		2293			2299			2298	w		
2295	m	2275	m		2275	w		2240	vw		
		2250			2248						
								1950	vvw		OH stretches lowered due to hydrogen bonding.
1765	vs	1950			1952	vvw		1880	vw		
1760	vs	1908	w		1860	w		1855			
1725	vs	1848			1852						
								1648	s		O–H–O bend. water of crystallization.
1645	vs	1650	not resolved		1651			1630	s		
1630		1335			1648	s					
					1638						
1572		—	—	—	1566	s	a_u	1575	s	b_u	
1549	s	—	—	—	1555	s	a_u	1570		a_u	ν_8, ν_2, ν_{10}, COO asymm. stretches.
1530		—	—	—	1533	s	a_u	1550	s	b_u	
								1540		b_u	
								1520		—	
1501		—	—	—	1502	s	a_u	1503	s	a_u	ν_{17}, ν_{18}, CH_2 bends.
1498	s	—	—	—	1499	s	—	1497		—	
1480		—	—	—	1487	s	a_u				

Table 2 contd

I.R. freq.cm^{-1} KBr Pellet spectrum due to authors	Int.	Single crystal I.R. freq.cm^{-1} (010) plate	Int.	Species	Single crystal I.R. Freq.cm^{-1} (001) plate b-axis	Int.	Species	Single crystal I.R. freq.cm^{-1} (001) plate a-axis	Int.	Species	Assignment
1465 1451 1420	s	— — —	— — —	— — —	1472 1455 1433	s s w	a_u a_u a_u	1473 1467 1450 1442 1425	s	a_u b_u a_u b_u b_u	ν_5, ν_6, ν_7, COO symm. stretches.
1406	s	—	—	—	1413	w	a_u	1415	s	a_u	ν_{19}. CH_2 bend.
1348 1280	m.br.ab. region	1325 1280	s.br.		1346	s	a_u	— 1294	— vvw	—	ν_{35} CH_2 deformations. ν_{36}
— 1182	— w	1186 1183	w w	— b_u	1189	w	a_u	1188 1182	w.br.	—	ν_{11}. C–OH stretch.
1071 1059	vw vvw	1075 1065	w w	b_u b_u	1072 1058	m.br.	b_u a_u	1070 1060	m.br.		ν_{27} C–OH oscillations. ν_{28}
969 950	w w	970 950	w vvw	b_u b_u	970 947	vw m	b_u a_u	970 950	vw w	b_u b_u	ν_{12} C–C stretches. ν_{13}
914 900	s	917 900	vvw w		916 912 900	w w w	a_u b_u a_u	915 900	w.br. vw	— a_u	ν_{21} ν_{22} COO deformations.
856 842	m	860 —	vw.br —	b_u —	857 849	w.br	a_u a_u	— —	— —	— —	ν_{23} ν_{24}
770 747	w vw	— 748	— w	— —	768 743	w.br w	— —	775 —	w.br —	— —	ν_{40} CH_2 rocking. ν_{41}
530 510	m.br. m.br.	520	m	—	528 519 498	w w w		529 522	w w	— —	ν_{29} C–C bends. ν_{30}
— 454	— w	464 —	w —	— —	— 458 452	— w	—	460 455 450	w w	— —	ν_{37} COO out of plane bends. ν_{38}
411	w	—	—	—	419	w		420	vw	—	ν_{13} C–C torsion.

split frequencies mentioned above. Of these two, the a component could be identified first since it should be present in (001) plate spectrum and should be absent in (010) plate. When once the a component was identified the remaining split component should be the b component. Since we have recorded the spectra of (001) plate with a and b axis parallel to the slit of the spectrophotometer, the assignments of the species have been done with ease. But in the 1300–1600 cm^{-1} region none of the single crystal spectra are resolved very well and so in this region assignments have been effected with the help of the KBr pellet spectrum. In the case of the spectrum of an unoriented specimen the symmetric species will usually appear with high intensity compared to the antisymmetric species of the same group or bond. This principle was used while making the assignments with the KBr pellet spectrum. It was not possible to assign the split components of some of the frequencies like ν_{40}, ν_{41} etc., to their species because of the fact, that the b-axis spectrum is taken with random orientation. Thus the split components of the available fundamentals of the citrate ion are assigned and the assigned frequencies are discussed below :

CH_2 *Frequencies* :

The stretchings of this group appear in the region 2937–2895 cm^{-1}; the bendings at 1501, 1480, 1406 cm^{-1} have split up as expected and their species are assigned. Four CH_2 bending frequencies (free state) are expected but we could identify only three in the KBr spectrum and this region is not resolved well in the single crystal spectra. The deformations appear at 1340, 1285 cm^{-1} and the rocking frequencies appear at 770, 747 cm^{-1}. The CH_2 group according to the crystallographic details on magnesium citrate, is known to be situated out of the back-bone plane and the frequencies pertaining to this group must appear in the spectra of both the C_s groups, as was observed.

COO *Group Frequencies* :

Stretchings of this group appear at 1572, 1549 and 1532 cm^{-1}, 1465 1445 and 1420 cm^{-1} and the deformations appear at 914, 900, 856, 842 cm^{-1}. The out of plane bendings appear at 453, 460 cm^{-1}. From the crystallographic details it is known that there are two COO groups in (010) plane which is the back-bone plane and the other COO group is in (001) plane which is perpendicular to the back-bone plane. These two planes represent two C_s groups. This group frequencies clearly proved that the point group C_1 consists of two C_s groups. The stretching region is not well resolved but the other regions are in conformity with a C_s site symmetry.

C–OH *Frequencies* :

The frequencies at 1182, 969, 1071, 1065 cm^{-1} are attributed to the vibrations of this group. The 1182 cm^{-1} is identified to be the stretching frequency of this group. The other frequencies are due to the bending modes of this group.

According to the structural details, this group vibrations should appear only in (001) plate spectrum, since this group is in the (001) plane. But C–OH group frequencies may also appear in (010) plate spectrum, since the O–H–O type of bonds attached to some *C*-atom also will have *C*–OH group vibrations.

C–C *Frequencies* :

The frequencies of this group appear at 950, 530, 523, 508 cm^{-1} and the split components are identified and duly assigned.

C–C *Torsional Vibrations* :

These are due to torsional vibrations of the molecular frame and identified at 420 and 411 cm^{-1}.

Hydrogen Bond Frequencies :

The frequency regions of this group were reported by us in the previous paper on potassium citrate at 2370, 1760, 1645 cm ^{1}. The O–H–O frequencies of the polycrystalline spectrum have split up into a number of components in the present single crystal spectra. Due to the lack of full details regarding the number and arrangement of hydrogen bonds, we were unable to derive maximum useful information from the spectra and could only identify the regions.

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